A Preliminary Investigation of the Interfacial and Dielectric Properties of Polyhedral Oligomeric Silsesquioxane Polymer Blends

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FOREWORD

This document reports the first in-house investigations of the interfacial and dielectric properties of Polyhedral Oligomeric Silsesquioxane (POSS) polymers and blends as synthesized by Air Force Research Laboratory (AFRL) scientists at Edwards AFB, California and Wright-Patterson AFB, Ohio. Work at AFRL/Edwards Site was performed as JON: 1R2RRD67. Dr. Patrick Mather was the project manager.

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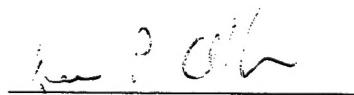
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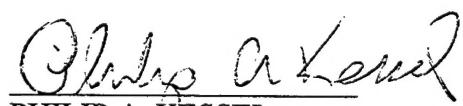
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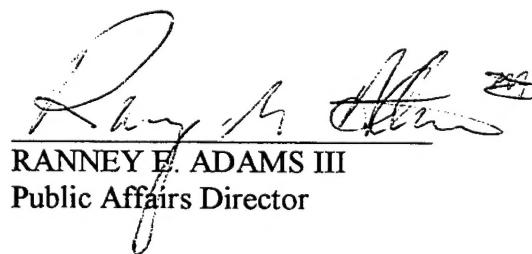
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13. ABSTRACT (MAXIMUM 200 WORDS)

The interfacial tension and dielectric properties of Polyhedral Oligomeric Silsesquioxane (POSS) have been Investigated. POSS end-capping of a semiflexible liquid crystalline polymer lowers the interfacial tension between the parent liquid crystalline polymer (LCP) and poly(dimethyl siloxane) PDMS. The interfacial tension lowered with time, most likely because of POSS segragation to the LCP/PDMS interface. The dielectric properties of POSS compounds in the X-band region were measured. POSS appears to generally raise the dielectric constant while not impacting the loss tangent. POSS compounds were also seen to have higher hardness than the non-POSS resin.

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GLOSSARY

amu	atomic mass unit
CCD	Charge Coupled Device
DSC	Differential Scanning Calorimetry
IFR	Imbedded Fiber Retraction
K_m	Rayleigh instability wavenumber
LCP	liquid crystalline polymer
MW	molecular weight
mN	milli-Newton
m	meter
N_2	nitrogen gas
nm	nanometer
PDMS	poly(dimethyl siloxane)
POSS	Polyhedral Oligomeric Silsesquioxane
q	Rayleigh instability growth rate
R_e	effective radius
R_o	initial radius
T_g	glass transition temperature
TGA	thermogravimetric analysis
α	fiber diameter time function
η_o	zero shear viscosity
η_f	fiber viscosity
η_m	matrix viscosity
Ω	proportionality function relating interfacial tension to physical dimensions of instability
σ	interfacial tension
χ	Flory interaction parameter

1.0 INTRODUCTION

In an attempt to meet Air Force demands for a new generation of lighter weight and higher performance polymeric materials, for the past decade the Air Force Research Laboratory (AFRL) has pursued the development of a new chemical feedstock technology based on Polyhedral Oligomeric Silsesquioxane (POSS). POSS chemical technology is derived from the same silane feedstocks that are currently used to prepare conventional bulk silicone resins[1]. However, the technology is unique in that POSS reagents are physically large three-dimensional cages (approximately 15Å in diameter and 1000 atomic mass units (amu) in weight) that are nearly equivalent in size to most random coil polymer dimensions, and their composition is hybrid, i.e., intermediate between inorganic and organic (*vide infra*). Recently bulk-scale preparative methods and a catalogue of POSS monomers (nano-structured hybrid chemical feedstocks) have been established.
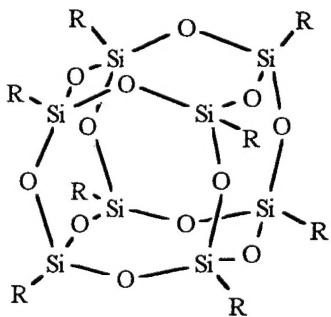
Figure 1
POSS Molecule Geometry

The scope and range of property enhancements in POSS-based nanocomposite plastics are only now beginning to be identified. Despite a dependence on composition, polymer type, and architecture, a few general property enhancement trends have become apparent. POSS incorporation effectively reduces polymer flammability[2], decreases thermal conductivity, improves oxidation resistance[3], increases permeability to gases[4], increases glass transitions[5], improves heat distortion and melt strengths[6], and significantly increases moduli. Although highly dependent upon molecular weight, processing, molding conditions, and composition, the tensile properties of POSS-plastics are nearly equivalent to those of the purely organic resin. Interestingly nano-

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composites derived from POSS do not appear to suffer from decreases in shear strength, as do the exfoliated/intercalated clay-based nanocomposite systems[*].

It is desirable to enhance the performance of existing polymer resin systems through blending or compounding with additives that target specific properties, such as glass transition temperature (T_g) or heat distortion temperature, without detrimentally impacting other properties, such as tensile strength or melt viscosity (for ease of processing). In this document, the results of two investigations are reported: 1) the effect of POSS incorporation on the interfacial properties in a hybrid polymer system; and 2) the effect of POSS incorporation in commercial resins on the dielectric properties, specifically loss tangent and dielectric constant.

2.0 INTERFACIAL TENSION MEASUREMENTS

2.1 Introduction

The development of polymer blends containing liquid crystalline polymers has seen tremendous activity in the polymer science and engineering community during the past 15 years. The practical reasons for this are twofold. First, liquid crystalline polymers (LCPs) as a minor phase in a polymer blend offer the desirable capability of reinforcing a matrix polymer of lower strength in a manner similar to short or continuous fiber composites. Secondly, the relatively high cost of commercially available LCPs can be substantially offset by a material strategy in which the material requirements of an application are met by the minimum weight fraction of LCPs. Indeed, it has become quite common throughout the plastics industry to attempt property tailoring by blending immiscible polymers, and LCP blends are following this same trend.

For LCP-blends to perform optimally, it is necessary for the blend to contain strong adhesion between the polymer matrix and the reinforcing LCP phase. One of the shortcomings of liquid crystalline polymers has been their poor adhesion to metal surfaces, to other polymers, and to LCPs (reflected in their poor weld-line strength)[7]. Alternatively, *in-situ* composite reinforcement with LCPs can occur if the blend contains reinforcing LCP fibrils with aspect ratios on the order of 100[7]. Methods for improving inter-phase adhesion in polymer blends have typically employed

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[*] Shelley, J., Mather, P.T., and Chaffee, K.P., work in progress

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the use of block copolymers[8]. Recently random copolymers have been identified as a more efficient means to enhance polymer-polymer adhesion[9,10].

To our knowledge, only one research group has attempted to measure interfacial tension between LCPs and isotropic thermoplastics. Their work measured interfacial tension by separately measuring dispersive and polar contributions to interfacial tension and computing the total interfacial tension using the harmonic mean approximation. Most polymer-polymer pairs feature interfacial tension values on the order of 1-10 mN/m[10]. These values are affected by contributions from both polar interactions and dispersive (London) forces between neighboring chemical groups at the interface. To our knowledge only two measurements of interfacial tension between thermotropic LCPs and isotropic polymers have been reported. In both cases, interfacial tensions greater than 20 mN/m were observed. Potential explanations cited the large solubility parameter difference between the groups present in aromatic polyesters and other polymers, leading to a large Flory χ parameter, and potential entropic effects arising from the conformational incompatibility between flexible polymers and rigid polymers[11].

Since it has been shown that end-groups play a large role in determining interfacial properties for other polymers[11], this work attempted to modify these properties in LCPs through end-groups. A unique thermotropic liquid crystalline polymer that has been end-capped with the silicon-oxygen cage POSS (Polyhedral Oligomeric Silsesquioxane) molecule is characterized in an effort to modify properties such as surface tension, adhesion to other materials, and thermal stability.

2.2 Interfacial Tension Experimental Procedures

The synthetic route utilized for production of the POSS end-capped LCP is shown schematically in Figure 2, details of which will appear in the literature[*]. The weight fraction of the POSS end-capped Molecule 4 was about 10% of the total yield. Thermal analysis of the end-capped LCP was performed using a DuPont Instruments differential scanning calorimeter (Model 912) and a DuPont Instruments thermogravimetric analyzer (Model 951). Both experiments were conducted with temperature sweeps of 10°C/min under a constant flow of dry nitrogen gas.

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* Mather, P.T., Chaffee, K.P., Haddad, T.S., manuscript in preparation

Thermal analysis experiments were complemented with hot-stage microscopy observations using an Aus Jena polarizing microscope along with a convective heating-stage (Fluid, Inc.).
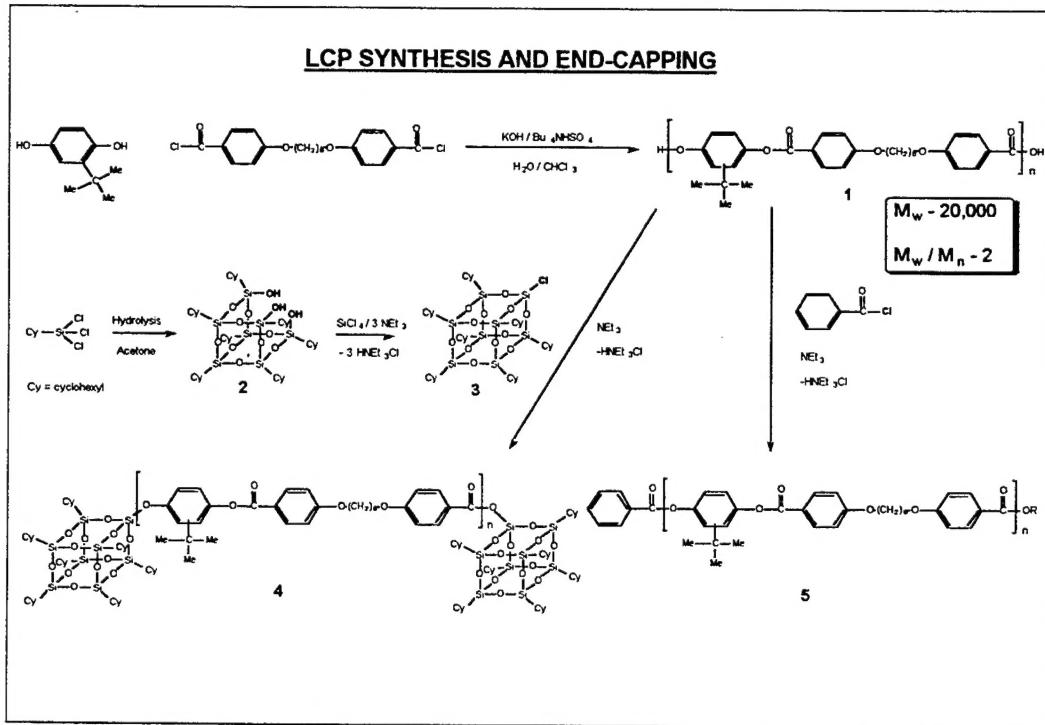
Figure 2
Synthetic Route to LCP Production

Disks of the polymers were prepared for rheological analysis from approximately 1 gram of the powdered polymer material (25-mm diameter by approximately 1-mm thick) using a Tetrahedron compression mold at 16 MPa and 260°C for 15 minutes. Rheological properties were determined using a Rheometrics RMS-605 rheometer in the parallel plate geometry for dynamic testing, with the amplitude selected to maximize the torque signal while maintaining linear viscoelastic response. Samples were heated by forced convection of dry N_2 gas and the temperature was controlled to within ±0.5°C.

Apparent interfacial tension measurements were made for both the parent LCP and the end-capped LCP using the breaking thread method (BTM)[12] and the imbedded fiber retraction method (IFR)[12,13]. In the thread break-up technique, the interfacial tension between a fiber of one polymer and the matrix of another polymer drives a surface instability leading ultimately to the formation of polymer droplets. The kinetics of this instability have been studied for viscous liquids, but not

for LCPs (some modifications exist due to curvature elasticity). For comparison, we apply the viscous analysis and report apparent interfacial tensions with poly(dimethyl siloxane) (PDMS).

Fibers of each LCP were spun from the melt at 200°C using a bench-scale fiber-spinning apparatus built in-house. A 343-µm diameter spinneret with a length/diameter ratio (L/D) of 5 was used. Fibers of uniform diameter and aspect ratio (length/diameter) of approximately 100 were encapsulated in a PDMS matrix (Mw = 400,000, η_o = 3,200 Pa s at 180°C) at room temperature. The encapsulated fibers and matrix were heated from room temperature to 180°C in a convective heating stage (Fluid, Inc.) using a rapid heating rate of 100°C/min to minimize shape change prior to the isothermal testing conditions. The breaking-thread process (a so-called "Rayleigh instability) was observed *in-situ* with an Aus Jena Jenalumar polarizing microscope, using light polarized normal to the fiber axis and viewed with no analyzer. This optical configuration was chosen because it yielded high contrast between the fiber and matrix for accurate shape measurements. A Charge Coupled Device (CCD) camera was used in conjunction with a frame grabber (Data Translation DT3851) to digitize and analyze fiber diameter undulations from the images once they were archived to SVHS videotape. Images evenly spaced over time were processed to determine the growth rate, q, of the Rayleigh instability. The variation in fiber diameter along the fiber axis at each time was fit to the following function,

$$a(x,t) = O + \alpha(t)\cos(k_m x + \phi), \tag{1}$$

where x is the axial position, O is the offset in the direction perpendicular to the fiber axis, k_m is the instability wave number, and ϕ is an arbitrary phase. The growth rate, q, was determined from a line fitted to the $\ln(\alpha/\alpha_o)$ versus t data. Use of the analysis of Tomotika[14] allows determination of interfacial tension from the growth rate and viscosity data.

Measurement of interfacial tension using Imbedded Fiber Retraction (IFR) was performed in a similar manner, only using a different starting geometry and applying a different fluid mechanics solution to the shape evolution to extract interfacial tension. In particular, fibers with an aspect ratio of less than 5 were imbedded in the PDMS at room temperature and then heated to 180°C at 100°C/min. The evolution of the fiber shape was monitored with video microscopy. Videotape images were then digitized and analyzed to yield the fiber length, diameter, and effective radius,

R_e. Fitting this shape evolution data to the model calculations of Carriere and Cohen[13] involves plotting a function versus time with the slope proportional to the interfacial tension.

2.3 Results and Discussion

The Differential Scanning Calorimetry (DSC) results show that the addition of the POSS end caps only slightly modifies the nematic-isotropic transition by reducing the latent heat and increasing the nematic-isotropic transition temperature. The glass transition temperature remains essentially unchanged on end capping with POSS at approximately 92°C. The nematic phase observed between crossed polarizers appears similar for the capped and uncapped polymers, showing a birefringent melt containing a large concentration of disclinations.

Samples of LCP end capped with benzoyl chloride (tBHQ6-*e*-B) and samples terminated with POSS-chloride (tBHQ6-*e*-POSS), were examined using hot-stage photo-microscopy for temperatures ranging from room temperature to 250°C. Prior to microscopic observation, the samples were prepared on a temperature-controlled stage within a Plexiglas N_2-purge chamber. Polymer was placed on a 25-mm diameter glass cover slip and then compressed to a thin film with a second, 18-mm diameter, cover slip. Once this film was relatively transparent to the eye, the sample was removed from the hotplate and cooled to room temperature within the nitrogen environment. For both tBHQ6-*e*-B and tBHQ6-*e*-POSS, sample preparation was performed at 180°C.

Thermogravimetric analysis (TGA) was performed on tBHQ6-*e*-B and tBHQ6-*e*-POSS. While the decomposition temperature remains unchanged upon end capping with POSS, $T_{decomp} =$ 423°C for tBHQ6-*e*-POSS while $T_{decomp} =$ 433°C for tBHQ6-*e*-B, the char yield at 750°C is increased moderately with POSS addition from 13% for tBHQ6-*e*-B to 20% for tBHQ6-*e*-POSS.

The rheological properties of the thermotropic LCP were greatly modified by the incorporation of POSS. Specifically, the value of the viscosity was much larger for the POSS end-capped polymer.

The instability wavelength determined from the Rayleigh instability wavenumber (K_m) implies a viscosity ratio of $\eta_f / \eta_m \sim 1/10$, consistent with preliminary rheological measurements of this value. The apparently enhanced viscosity ratio is believed to be reflective of dynamics internal to the nematic fiber, which are more complicated than the simple case of a viscous thread.

The use of the zero shear dynamic viscosity for the textured LCP is perhaps inappropriate, and perhaps monodomain splay/bend viscosity[15] better reflects the material's resistance to the Rayleigh instability. A lower growth rate is expected for this system in which Frank bend and splay elasticity resists director gradients away from the oriented fiber state. In fact it seems reasonable that in the limit of high bend/splay elasticity or high orientation, the Rayleigh instability may not occur at all.

Using the equation,

$$\sigma = 2 \cdot R_o \cdot \eta_m / \Omega \qquad (2)$$

where R_0 is the initial fiber radius, η_m is the matrix viscosity (32,000 Poise), and Ω is a tabulated function dependent on viscosity ratio and instability wavelength, the interfacial tension for the as-synthesized LCP in PDMS is found to be 23.2 dyn/cm. It is important to note that the viscosity ratio corresponding to the measured instability wavelength from the Tomotika solution to the viscous-viscous Rayleigh instability was substantially larger than the actual value. This indicates a possible inadequacy of the Tomotika analysis to describe the observed instability growth, and is consistent with the discussion on the effect of molecule orientation on the dynamics of the process.

A representative time sequence for the imbedded fiber retraction experiments is shown in Figure 3, with the time axis being vertical.

In this technique, an effective radius parameterizes the evolving shape to extract vales of interfacial tension for a retracting cylinder with hemispherical end caps. In particular, the IFR analysis yields plots of a function that depends on the effective radius and final droplet radius. When this function is plotted versus time, the slope depends on interfacial tension as shown in Equation 3.

$$\sigma_{12} / \left[\left(\{ \eta_m + 1.7 \eta_f \} / 2.7 \right) R_o \right] \qquad (3)$$

where η_m is the viscosity of the matrix material, η_f is the viscosity of the fiber material, and R_o is the initial diameter of the fiber. As can be seen in Figure 4, the high interfacial tension for tBHQ6-e-B manifests itself as a large slope in the $f(R/R_o)$ versus time curve. On the other hand, the slope of the $f(R/R_o)$-t curve continuously decreases with time for tBHQ6-e-POSS in PDMS apparently indicating a continual decrease in interfacial tension with time. In particular the initial interfacial

tension of 25.4 mN/m is reduced, over the period of 1.5 hours to 0.23 mN/m, a substantial reduction in interfacial tension. We hypothesize that this reduction is due to the changing segmental composition profile across the LCP/PDMS interface; i.e., POSS macromers are likely diffusing to the interface since the POSS dislikes PDMS much less than it dislikes the aromatic polyester. This is shown schematically in Figure 5.
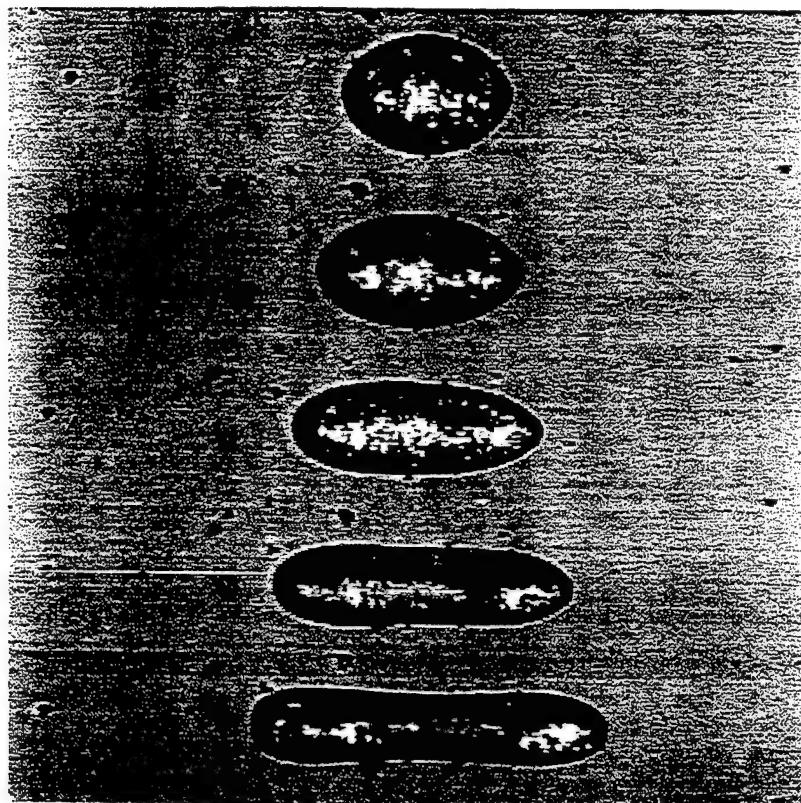

Figure 3

Time Evolution for the IFR of the Non-POSS LCP

For all of the various available experimental methods to measure interfacial tension, the value derived is only as accurate as the model is applicable to the system being studied. For example, for the spinning drop method analysis the limiting case for a final cylindrical specimen would be straightforward, but the limiting shape is rarely achieved experimentally. The lack of monodisperse size distributions renders the dynamic shear oscillation theories at least somewhat inaccurate. Techniques that rely on maintaining the molten blend at elevated temperatures while the dispersed phase reaches an equilibrium shape, such as pendant drop tensiometry, are

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problematic for systems where polymer degradation can occur, especially considering that it may take hours to reach equilibration.
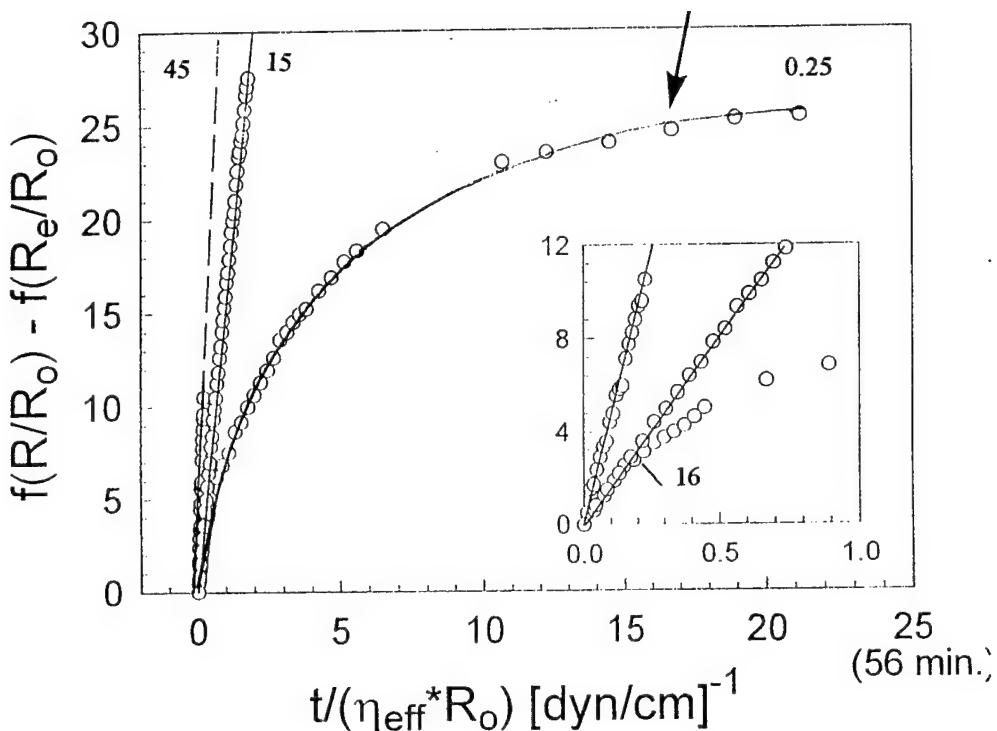

Figure 4
Shape Factor Data

The morphology of an immiscible polymer blend is determined by the chemical constitution of the components, their rheological properties, the interfacial tension between the phases, and the thermomechanical history. In the dispersed phase the time evolution for the shape and size in the molten blend as it responds to a shear field at elevated temperatures is dependent on the relative strength of the viscoelastic to the interfacial forces. Interfacial tension is typically measured by observing the shape changes or equilibration of the dispersed phase, or by measuring the energy required to deform the dispersed phase from its equilibrium configuration. The information collected such as the final droplet shape (pendant drop tensiometry), dimensional changes as a function of time (IFR and thread breakup), or the relaxation spectrum (dynamic shear oscillation) are then analyzed with respect to a theoretical model.

Imbedded fiber retraction, thread breakup, dynamic shear oscillation[16,17] and pendant drop tensiometry[18] are methods that have been used to measure interfacial tension between immiscible polymers. All of these techniques assume an isotropic viscous dispersed phase encapsulated in an isotropic viscous continuous matrix. For the case in which one of the components is in the nematic liquid crystalline phase, linear viscoelastic measurements may be better since the disclination density can remain constant throughout the test. In the thread break-up experiment the large molecular orientation resulting from fiber spinning seems to relax and distort in response to the internal flow patterns.

A droplet relaxation method similar in principle to the imbedded fiber retraction method was attempted to measure interfacial tension to avoid effects of orientation relaxation for oriented fiber starting material. Here, our intent was to determine a characteristic droplet relaxation time and to use the result to compute interfacial tension[17]. However, spherical droplets of the LCPs did not deform to well-defined ellipsoids, but were clearly thinner in the gradient direction than in the vorticity direction.

RCP

Time

POSS-Terminated
LCP

Low Interfacial Energy
High Interfacial Strength
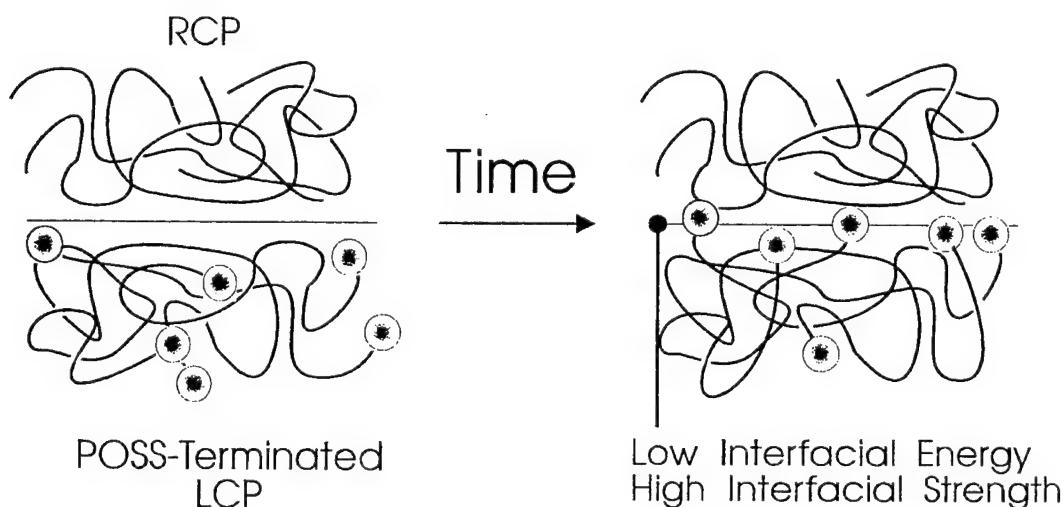
Figure 5

Schematic for Compositional Changes at Interface

3.0 DIELECTRIC PROPERTIES

As the military moves towards higher speed platforms, existing sensor windows will be insufficient to meet mission requirements. Although ceramic materials possess the desired thermal and mechanical properties (in regards to erosion/hardness), they have high dielectric constants that lead to design and component fabrication difficulties. Slip cast fused silica, with the lowest dielectric constant (near 4), has low strength and erosion properties. Polyhedral Oligomeric Silsesquioxane, POSS, is a hybrid material consisting of both organic and inorganic moieties. POSS has demonstrated that it can lower density (and the dielectric constant) while increasing thermal properties such as T_g.

Twelve POSS containing polymer blend nanocomposite plaques were fabricated and tested for hardness and dielectric properties. The polymer matrices examined were polystyrene, Parmax™ 1000 (a polyarylene from Maxdem Inc.), nylon-6, a poly(carbosilane), and a poly(siloxane) and Geobond™ (a ceramic from Geobond Inc.). POSS and clay content, typically 2% by weight, was much higher for the Parmax™ composites.

POSS incorporation decreases the durometer hardness value of the polymer matrices by approximately 3-5%. This is less than achieved by incorporating clay as a reinforcing agent. This is not a positive result. Indeed, the poly(carbosilanes) and poly(siloxanes) were too brittle to be machined to the 0.030-in. thickness required to measure the loss tangents. Erosion resistance is expected to scale with hardness. A decrease in this hardness would imply that the POSS containing materials would have a lower resistance to rain and dust erosion.

The dielectric constant and loss tangent in the X-band frequency range (8-12 GHz) were largely unaffected by POSS incorporation. Whereas the dielectric constants for all the materials studied were in an acceptable range (3's for the polymers and 5.65 for the Geobond™), only the Poly-X™ based composites had a sufficiently low loss tangent. At 35% weight loading of POSS, the loss tangent for the Poly-X™ material increased from 0.0054 to 0.0076. These results are summarized in Table 1.

Table 1. POSS Composite Dielectric Properties

Material	Hardness	Dielectric Constant	Loss Tangent
Polystyrene	86D	2.49	0.0005
Parmax™-1000	94.2D	3.13	0.0054
65%Parmax™-1000/35%POSS	91.0D	3.42	0.0076
65%Parmax™-1000/35%Clay	87.0D	*	*
Nylon 6	81.4D	3.00	0.010
Nylon 6/2%POSS	78.0D	2.99	0.010
Nylon 6/2%Clay	78.8D	3.03	0.012
Geobond™	88.0D	5.65	0.013
HPCS	19.6D	3.42	0.110
PI/HPCS	54.4D	2.86	0.070
PolySiloxane	25.4D	*	*

The samples marked with an asterisk had insufficient mechanical properties to allow for production of a sample of the proper geometry to allow for dielectric measurements.

4.0 CONCLUSIONS AND RECOMMENDATIONS

The interfacial and dielectric properties of Polyhedral Oligomeric Silsesquioxane based polymers and blends have been investigated. POSS has been shown to render inorganic/organic polymer blends compatible by lowering the interfacial tension between these two materials. This will allow dispersed phases containing POSS to retain their shape and to retain their desired properties during processing or through another thermal cycle. Although the impact on hardness was unfortunate, using copolymers of POSS with a suitable engineering thermoplastic could possibly alleviate this problem.

The authors recommend that further investigation of the impact of POSS on fundamental physical and chemical properties of blends and copolymers. The extent to which this new polymer building block can increase the usage of polymeric materials in the aerospace community will depend on understanding the relationships between POSS containing materials' microstructure and their physical and chemical properties.

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